

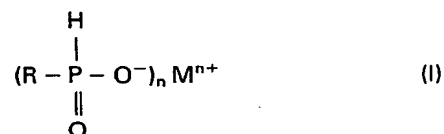
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(54) Fungicidal compositions

(57) Fungicidal compositions comprising, as active ingredient a synergistic mixture of:-

A) - at least one fungicide of the phosphite type of the general formula:



wherein R = OH, alkyl (C<sub>2</sub>-C<sub>4</sub>) or alkoxy (C<sub>2</sub>-C<sub>4</sub>), M = H (if R = OH), an alkali metal, an alkaline earth metal or aluminium, and R may also be ONa when M = Na; and n = 1 to 3, and

B) - cymoxanil, are described.

These compositions can be used to protect plants against fungal diseases, in a preventive or curative treatment.

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## SPECIFICATION

## Fungicidal compositions

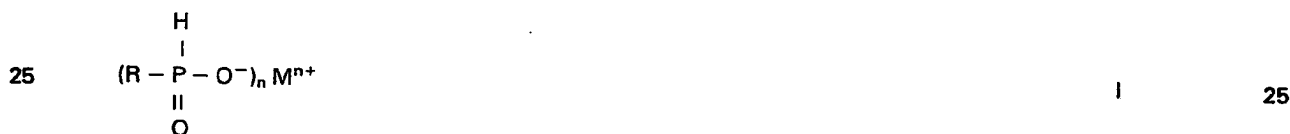
- 5 The present invention relates to new compositions for protecting plants against fungal diseases, and in particular to compositions comprising, as active ingredients, a fungicide of the phosphite type and 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea. 5

It is known to use systemic fungicides to protect plants against fungal diseases. In particular, phosethyl-Al (the common name for aluminium tris-O-ethyl-phosphite or aluminium ethyl-phosphate) is used for 10 protecting vines and other plants against *Phycomycetes*. This product has a remarkable action in preventive treatment and a secondary curative activity at its normal use dose. It is usually employed in a mixture with contact fungicides. 10

The fungicide 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea (hereinafter referred to as "cymoxanil" which has a limited systemic action and a secondary curative action, is also used. This product is generally 15 used against *Phycomycetes* in a mixture with a contact fungicide in order to improve its persistence. 15

It has now been found, surprisingly, that if phosethyl-Al or its homologous derivatives as hereinafter defined are used in combination with cymoxanil, the mixtures have a remarkable synergistic action, especially curative action, against fungal diseases.

- The present invention accordingly provides fungicidal compositions which comprise, as active ingredient, 20 a mixture of 20
- A) at least one fungicide of the phosphite type of the general formula:



wherein R is an OH group, an alkyl group containing from 2 to 4 carbon atoms or an alkoxy group containing 30 from 2 to 4 carbon atoms, M is a hydrogen atom (only if R is itself an OH group) or an alkali metal, alkaline earth metal or aluminium atom, and R may also represent ONa when M is a sodium atom; and n is an integer from 1 to 3, and 30

-B) 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea.

Amongst the compounds of the general formula I, monosodium and disodium phosphites, and more 35 especially aluminium tris-O-ethyl-phosphonate, are preferred. The weight ratio of B/A is advantageously between 1/100 and 20/100 and preferably between 2/100 and 10/100. The compositions according to the invention can also comprise other active ingredients, for example from one to three contact fungicides chosen from the group consisting of antimildew compounds such as fungicides based on copper, maneb, 40 zineb and zinc metiram (complex of zineb and polyethylenethiuram disulphide), and more especially folpet, captafol and mancozeb or fungicides which are active against other diseases such as botrytis and black rot. 40

The mixtures according to the invention can be prepared as a ready-to-use formulation or can be mixed for immediate use.

The following non-limitative example illustrates the invention and shows how it can be put into practice.

#### 45 Example 45

A mixture of phosethyl-Al (A') and cymoxanil (B) in a weight ratio of B/A' = 6/100 is prepared.

The mixture formulated in this way is used *in vivo* against *Plasmopara viticola* on vine plants in a greenhouse (curative treatment).

Vine plants (Chardonay variety), cultivated in pots, are treated on both sides of their leaves by spraying 50 with an aqueous suspension, at the desired dilution, containing active ingredients to be tested, respectively phosethyl-Al by itself, in the form of a wettable powder containing 80% by weight of active ingredient, cymoxanil by itself, in the form of a ready-to-use wettable powder containing 50% by weight of active 50 ingredient, and a mixture of both wettable powders.

The suspension formed in this way is diluted with water, respectively one-fold and two-fold, to give three 55 spraying emulsions having the desired concentration of active ingredients to be tested. Spraying is carried out under conditions such that the spraying of a suspension having a concentration of 1 g/litre corresponds to the application of about 2 microgrammes of active ingredients per cm<sup>2</sup> of area of plant leaf. 55

In each case, two suspensions each containing one of the active ingredients A' and B at the concentration at which they are present in the mixture are prepared in the same way.

60 A few days (n = 1 to 3 days) before spraying the active ingredients, the plants were contaminated by spraying the underside of the leaves with an aqueous suspension containing about 80,000 units/cc of spores of *Plasmopara viticola*, which is responsible for vine mildew. The pots were then placed in an incubation cell for 48 hours at 100% relative humidity and at 20°C. 60

The plants are checked 9 days after contamination. The check is made by measuring the sporulated areas 65 as a percentage relative to the control, the total area of which is sporulated. 65

The results are recorded in the table which follows:

5	Product	Dose g/l	Curative Efficacy With Treatment n Day(s) After Contamination			5
			1	2	3	
10	Phosethyl-Al (A')	0.5	0	0	0	10
		1	0	0	0	
		2	70	35	0	
15	Cymoxanil (B)	0.03	15	15	0	15
		0.06	75	75	0	
		0.12	100	80	25	
20	Phosethyl-Al (A') + Cymoxanil (B)	0.5				20
		+0.03	90	75	75	
		1				
		+0.06	97	95	85	
		2				
		+0.12	100	97	85	

25 This table clearly shows that the curative activity of the mixtures at three different doses is superior or very superior to the sum of the activities of phosethyl-Al and cymoxanil taken separately. The protection obtained is still virtually total after 2 days and still good after 3 days, the constituents being inactive in the latter case when they are used separately.

30 This example shows the excellent fungicidal activity of the compositions according to the invention which can be used on various families of phytopathogenic fungi, such as e.g. Phycomycetes, in a preventive or curative treatment.

35 For their use in practice, the compounds according to the invention are not generally employed by themselves. Most frequently, they are used in compositions which comprise, in addition to the active ingredient, an inert carrier (or diluent) and/or a surface-active agent which are compatible with the active ingredient.

These compositions also form part of the present invention. They usually contain from 0.001 to 95% by weight of active ingredient. They generally contain between 0.1% and 20% by weight of surface-active agent.

40 In the present account, the term "carrier" denotes an organic or inorganic, natural or synthetic material with which the active ingredient is combined in order to facilitate its application to the plant, to seeds or to the soil. This carrier is therefore generally inert and it must be acceptable in agriculture, in particular on the plant treated. The carrier can be solid (e.g. clays, natural or synthetic silicates, silica chalks, resins, waxes and solid fertilisers) or liquid (e.g. water, alcohols, ketones, petroleum fractions, aromatic or paraffinic hydrocarbons, chlorohydrocarbons and liquefied gases).

The surface-active agent can be an emulsifying, dispersing or wetting agent of ionic or non-ionic type.

45 Examples which may be mentioned are polyacrylic acid salts, lignosulphonic acid salts, phenolsulphonic or naphthalenesulphonic acid salts, polycondensates of ethylene oxide with fatty alcohols, fatty acids, fatty amines or substituted phenols (in particular alkylphenols, arylphenols or styrylphenol), salts of sulphosuccinic acid esters, taurine derivatives (in particular alkyltaurates) and phosphoric acid esters of condensates of ethylene oxide with alcohols or phenols. The presence of at least one surface-active agent is generally

50 essential, especially if the inert carrier is not soluble in water and if the vehicle of application is water.

The compositions used in the invention can be in a fairly wide variety of solid or liquid forms.

As forms of solid compositions there may be mentioned dusting powders or sprinkling powders (with an active ingredient content which can range up to 100%) and granules.

55 As forms of liquid compositions or compositions which are to be made up into liquid compositions on application, there may be mentioned solutions, in particular water-soluble concentrates, emulsifiable concentrates; emulsions, suspension concentrates, aerosols, wettable powders (or spraying powders) and pastes.

60 The emulsifiable or water-soluble concentrates most frequently comprise 10 to 80% by weight of active ingredient, and the emulsions or solutions which are ready for application contain 0.001 to 20% by weight of active ingredient. In addition to the solvent, and where necessary, the emulsifiable concentrates can contain 2 to 20% by weight of suitable additives such as stabilisers, surface-active agents, penetrating agents, corrosion inhibitors, dyestuffs and adhesives. Starting from these concentrates, emulsions of any desired concentration, which are particularly suitable for application to the leaves, can be obtained by dilution with water.

65 The suspension concentrates, which can also be applied by spraying, are prepared so as to give a stable

fluid product which does not form a deposit, and they usually contain from 10 to 75% by weight of active ingredient, from 0.5 to 15% by weight of surface-active agents, from 0.1 to 10% by weight of thixotropic agent, from 0 to 10% by weight of suitable additives such as anti-foam agents, corrosion inhibitors, stabilisers, penetrating agents and adhesives, and, as the carrier, water or an organic liquid in which the active ingredient is sparingly soluble or insoluble; certain organic solids, or inorganic salts, can be dissolved in the carrier in order to assist in preventing sedimentation or to act as anti-freeze agents for the water.

The wettable powders (or spraying powders) are usually prepared so as to contain 20 to 95% by weight of active ingredient, and they usually contain, in addition to the solid carrier, from 0 to 5% by weight of wetting agent, from 3 to 10% by weight of a dispersing agent and, where necessary, from 0 to 10% by weight of one or more stabilisers and/or other additives such as penetrating agents, adhesives, anti-caking agents and dyestuffs.

Various compositions of wettable powders are now given as examples:

#### Example 2

15	- active ingredients (6.5/100 mixture of B/A)	50 %	15
	- ethylene oxide/fatty alcohol condensate (wetting agent)	2.5%	
20	- ethylene oxide/styrylphenol condensate (dispersing agent)	5 %	20
	- chalk (inert carrier)	42.5%	
25	Another example of wettable powder has the following composition:		25

#### Example 3

30	- active ingredient (6.6/100 mixture of B/A')		30
	phosethyl-AL	50 %	
	cymoxanil	3.3%	
35	folpet	25 %	35
	- ethylene oxide/fatty alcohol condensate (wetting agent)	5.7%	
40	- ethylene oxide/styrylphenol condensate (dispersing agent)	6 %	40

To obtain these spraying powders or wettable powders, the active ingredient is intimately mixed with the additional substances in suitable mixers and the mixture is ground in mills or other suitable grinders. This gives spraying powders of advantageous wettability and suspendability; they can be suspended in water at any desired concentration and this suspension can be used very advantageously, in particular for application to the leaves of the plants.

As already stated, the aqueous dispersions and aqueous emulsions, e.g. compositions obtained by diluting, with water, a wettable powder or an emulsifiable concentrate according to the invention, are included within the general scope of the present invention. The emulsions can be of the water-in-oil or oil-in-water type and they can have a thick consistency such as that of a "mayonnaise".

The granules, which are intended to be placed on the soil, are usually prepared so as to have dimensions of between 0.1 to 2 mm, and they can be manufactured by agglomeration or impregnation. In general, the granules contain 0.5 to 25% by weight of active ingredient and 0 to 10% by weight of additives such as stabilisers, slow release modifiers, binders and solvents.

Compositions according to the present invention may also be in the form of dusting powders; thus, it is possible to use a composition comprising 50 g of active ingredient and 950 g of talc; it is also possible to use a composition comprising 20 g of active ingredient, 10 g of finely divided silica and 970 g of talc; these constituents are mixed and ground and the mixture is applied by dusting.

The invention also relates to a method for treating plants against attack by phytopathogenic fungi which comprises applying to these plants an effective amount of a mixture of A) at least one compound of general formula I (wherein R, M and n are as hereinbefore defined) and B) 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea in a composition according to the present invention, for example after contamination of the plants by the fungus or fungi. The term "effective amount" is understood as meaning a sufficient amount to enable

the fungi present on these plants to be controlled and destroyed. However, the use doses can vary within wide limits, according to the fungus to be combated, the type of crop and the climatic conditions.

# CLAIMS

- 5 1. Fungicidal compositions which comprise, as active ingredient a mixture of:- 5  
-A) at least one fungicide of the phosphite type of the general formula:-
- $$\begin{array}{c}
 \text{H} \\
 | \\
 (\text{R} - \text{P} - \text{O}^-)_n \text{M}^{n+} \\
 || \\
 \text{O}
 \end{array}$$
- 10 15 wherein R is an OH group, an alkyl group containing from 2 to 4 carbon atoms or an alkoxy group containing from 2 to 4 carbon atoms, M is a hydrogen atom (only if R is itself an OH group) or an alkali metal, alkaline earth metal or aluminium atom, and R may also represent ONa when M is a sodium atom; and n is an integer from 1 to 3, and -B) 1-(2-cyano-2-methoxyminoacetyl)-3-ethylurea, and optionally an inert carrier and/or surface active agent which is compatible with the active ingredient. 15
- 20 2. Compositions according to claim 1, wherein the weight ratio of B/A is between 1/100 and 20/100. 20  
3. Compositions according to claim 1 wherein the weight ratio of B/A is between 2/100 and 10/100.  
4. Compositions according to any one of claims 1 to 3, wherein the compound A is aluminium tris-O-ethyl-phosphonate.  
5. Compositions according to any one of claims 1 to 4, which also comprise, as active ingredient, from 25 one to three contact fungicides. 25  
6. Compositions according to any one of claims 1 to 4 which also comprise an antimildew contact fungicide.  
7. Compositions according to claim 6, wherein the antimildew contact fungicide is folpet.  
8. Compositions according to claim 6, wherein the antimildew contact fungicide is captafol.  
30 9. Compositions according to claim 6, wherein the antimildew contact fungicide is mancozeb. 30  
10. Compositions according to claim 6, wherein the contact fungicide is based on copper.  
11. Compositions according to any one of claims 1 to 10 which comprise from 0.001 to 95% by weight of active ingredient.  
12. Compositions according to any one of claims 1 to 11 which comprise from 0.1% to 20% by weight of 35 surface-active agent. 35  
13. Compositions according to any one of claims 1 to 12 in the form of dusting or sprinkling powders, granules, solutions, water-soluble concentrates, emulsifiable concentrates, emulsions, suspension concentrates, aerosols, wettable powders and pastes.  
14. Compositions according to any one of claims 1 to 10 in the form of dusting or sprinkling powders.  
40 15. Compositions according to any one of claims 1 to 10 in the form of emulsifiable or water-soluble concentrates comprising from 10 to 80% by weight of active ingredient. 40  
16. Compositions according to any one of claims 1 to 10 in the form of emulsions or solutions comprising from 0.001 to 20% by weight of active ingredient.  
17. Compositions according to any one of claims 1 to 10 in the form of suspension concentrates 45 comprising from 10 to 75% by weight of active ingredient, from 0.5 to 15% by weight of surface-active agent, from 0.1 to 10% by weight of thixotropic agent, from 0 to 10% by weight of suitable additives and, as carrier, water or an organic liquid in which the active ingredient is sparingly soluble or insoluble. 45  
18. Compositions according to any one of claims 1 to 10 in the form of wettable powders comprising from 20 to 95% by weight of active ingredient, from 0 to 5% by weight of a wetting agent, from 3 to 10% by 50 weight of a dispersing agent, from 0 to 10% by weight of one or more stabilisers and/or other additives, and a solid carrier. 50  
19. Compositions according to any one of claims 1 to 10 in the form of granules having dimensions of between 0.1 and 2 mm and comprising from 0.5 to 25% by weight of active ingredient and from 0 to 10% by weight of additives.  
55 20. Fungicidal compositions according to claim 1 substantially as hereinbefore described. 55  
21. Fungicidal compositions according to claim 1 substantially as hereinbefore described in Example 2 or

3.

22. A method for treating plants against attack by phytopathogenic fungi, which comprises applying to these plants an effective amount of a mixture of A) at least one compound of general formula I depicted in claim 1 (wherein R, M and n are as defined in claim 1) and B) 1-(2-cyano-2-methoxyiminoacetyl)-3-

5 methylurea in a composition according to any one of claims 1 to 21.

23. A method according to claim 22 in which the composition is applied after contamination of the plants with the fungus or fungi.

5

24. A method according to claim 22 for treating plants against attack by phytopathogenic fungi substantially as hereinbefore described.

10 25. A method according to claim 22 for treating plants against attack by phytopathogenic fungi substantially as hereinbefore described in Example 1.

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